Hydrogen-1, Carbon-13, and Aluminium-27 Nuclear Magnetic Resonance Studies of Complex Formation between Aluminium Isopropoxide and Ethylenediamine

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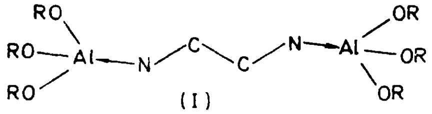
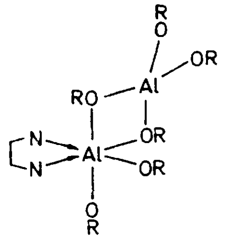
The interaction of $[Al(OPr^i)_3]_4$ with ethylenediamine in benzene solution has been studied using ^1H, ^{13}C, and ^{27}Al n.m.r. spectroscopy. The initial products appear to be a linear diadduct and a polymer, but other unidentified aluminium compounds may also be formed. There is no evidence to support the suggestion that significant amounts of complexes are formed containing five-co-ordinate aluminium.



(I)



(II)

A SOLID complex of composition $[Al(OPr^i)_3]_2 \cdot en$ can be isolated from solutions containing aluminium isopropoxide and ethylenediamine (en) and Bradley suggested that likely structures were (I) or (II).[1] In solution the molecular weight of the complex increases with concentration in a manner consistent with the formation of an octamer. Shiner and Whittaker[2] investigated the system in the presence of excess of en using ^1H n.m.r. and, from their analysis of the changes in chemical shift with temperature and of the exchange processes present, favour a structure containing five-co-ordinate aluminium in which the en bridges the aluminium atoms of the dimer moiety of (II). They suggested that such a complex could easily lead to polymeric species if the en ligand were to bridge different dimer units.

We have recently reported[3] that ^{13}C and ^{27}Al n.m.r. spectroscopy provide unequivocal evidence for the structure of aluminium isopropoxide tetramer. The present work was undertaken in the hope that the same multinuclear approach might resolve the controversy about the structure of its ethylenediamine complexes.

EXPERIMENTAL

Spectra were obtained as reported previously.[3] Solutions were made up by weight in dry benzene or carbon tetrachloride and were allowed to equilibrate over 3 d before measurements were made, except for the experiments where the progress of the reaction between the components was followed at time intervals following initial solution make-up. Low-temperature ^{13}C n.m.r. spectra were obtained in toluene.

RESULTS

Spectra were obtained for all three nuclides on a series of solutions of $[Al(OPr^i)_3]_4$ to which various amounts of en had been added and allowed to equilibrate. The ^{27}Al n.m.r. spectra are the most informative and are shown in Figure 1. The two lines in the pure tetramer spectrum are greatly reduced in intensity even on addition of small amounts of amine. The line from octahedrally co-ordinated Al is still visible but the broad low-field line is obscured by a much more intense and relatively narrow line which appears to originate also from four-co-ordinate aluminium.[4] Two

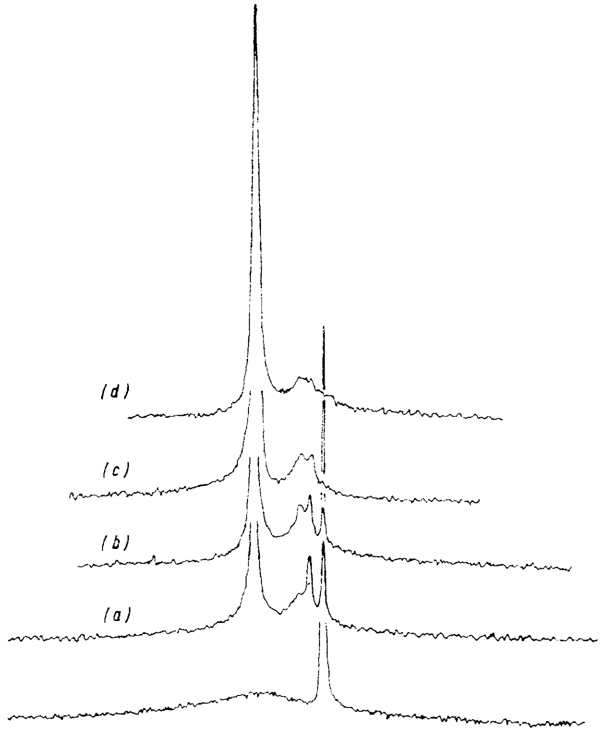


FIGURE 1 ^{27}Al N.m.r. spectra of equilibrated $[Al(OPr^i)_3]_4$–ethylenediamine mixtures: lowest curve, tetramer alone (the line due to octahedral Al is extended through the spectra above); (*a*) 3 Al atoms per N atom of en; (*b*) 1.65 Al atoms per N atom; (*c*) 1.04 N atoms per Al atom; (*d*) 1.93 N atoms per Al atom. The aluminium concentration was 0.276 mol kg^{-1} in each case

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[1] M. S. Bains and D. C. Bradley, *Canad. J. Chem.*, 1962, **40**, 2218.

[2] V. J. Shiner and D. Whittaker, *J. Amer. Chem. Soc.*, 1965, **87**, 843.

[3] J. W. Akitt and R. H. Duncan, *J. Mag. Resonance*, 1974, **15**, 162.

[4] J. W. Akitt, *Ann. Rep. N.M.R. Spectroscopy*, 1973, **5**, 465.

weak narrow lines can also be seen between the two major resonances. Interestingly, in trace (*d*) with excess of en the low-field line contains only 44% of the aluminium calculated to be present from the tetramer spectrum. The remaining aluminium is likely to be polymer, which should have an undetectably broad, presumably quadrupole-relaxed, line.

In addition, changes in solution composition after initial make-up were followed over a period of 8 h using ^{27}Al n.m.r. spectroscopy. Observations were made on both benzene and carbon tetrachloride solutions. The results were quantitatively the same for both solvents, although the lines in CCl_4 were much broader, the solutions being noticeably more viscous. The tetramer is consumed at a faster rate than the tetrahedral complex is formed (Figure 2), the difference presumably being due to the formation of the polymeric species. The quantities of polymer formed are different in the two solvents, most being present in benzene. The minor peaks were not observed and only appeared after a day or so, possibly as the polymer structure changes.

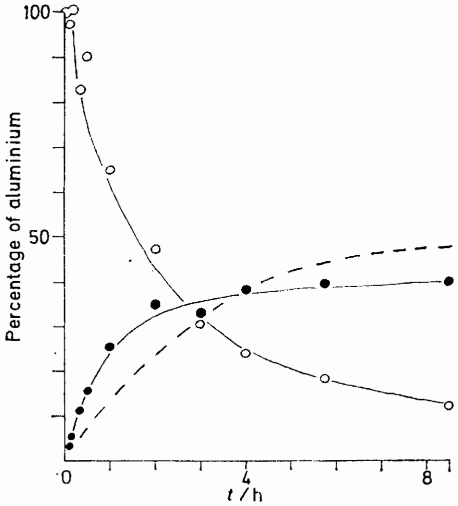

FIGURE 2 Variation of concentrations of species with time after addition of ethylenediamine to $[Al(OPr^i)_3]_4$: (○), percentage of Al as tetramer; (●) percentage of Al as tetrahedral complex; (— — —), percentage of Al 'lost'

The ^{13}C n.m.r. spectra were remarkably simple. The four lines due to the isopropoxide methyl groups of the tetramer were replaced by only one broad line, in the same position as the terminal isopropyl methyl groups. The methine carbon doublet was also replaced by a broad singlet. Because the resonances were broad, the effect of cooling was investigated. The high-field resonance split into an unequal doublet at −23 °C, but the splitting remained when the sample was allowed to return to room temperature.

Proton n.m.r. spectra in carbon tetrachloride were also simple. When en was in slight excess a single doublet was observed close to that of the terminal isopropoxide methyl resonances of the tetramer. The spectra obtained in benzene solutions were similar, although they also contained a resonance due to *ca.* 8% of an unidentified component.[5,6] Further addition of en resulted in an increase in complexity of the spectra, and it seems that the presence of an excess of en may not aid analysis of this system, contrary to what was assumed by earlier workers.[2] In addition the changes in chemical shift were small and are apparently affected more by solvent than by any other factor,[4] so that interpretation must depend heavily on the results from the other nuclides.

DISCUSSION

Several molecular species are obviously present in these solutions. One gives rise to a sharp low-field ^{27}Al line in a region of the spectrum where tetrahedral species are found, and this almost certainly arises from the diadduct (I). The asymmetric complex (II) or a five-co-ordinate complex would not give a narrow resonance since their aluminium atoms are in asymmetric environments and would have very much broader lines, such as, for example, the line arising from the tetrahedral aluminium atoms in the pure aluminium isopropoxide tetramer. Adduct (I) is thus most probably the one isolated by Bains and Bradley.[1] A structure with five-co-ordinate aluminium [2] is not supported by these spectra. Both the ambient ^{13}C and ^{1}H n.m.r. data are in accord with this conclusion since they indicate loss of bridging isopropoxy-groups on complex formation, although in view of the number of species present in the solutions the spectra are really too simple to be of much help in interpretation.

Adduct (I) forms polymeric species when dissolved at high concentration and the solutions made up as described here also appear to contain either the same or related species. In benzene solution the aluminium is distributed almost equally between the diadduct and the polymer and this, combined with Bradley's cryoscopic data, suggests that the polymer is a pentamer or hexamer. There is evidence also that the polymer composition changes with time as the minor lines appear to high field of the diadduct resonance. The unusual non-reversible splitting of the ^{13}C resonance which occurs on cooling also suggests that a variety of structures may occur. Unfortunately no definitive information can be obtained from the spectra about the constitution of the polymer (or polymers). It must almost certainly contain bridging isopropoxy-groups, although these are not evident in the ^{1}H or ^{13}C spectra, indicating that intramolecular terminal–bridge propoxy-exchange probably takes place.

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[5] V. J. Shiner, D. Whittaker, and V. F. Fernandez, *J. Amer. Chem. Soc.*, 1963, **85**, 2318.

[6] J. S. Oliver, P. K. Phillips, and I. J. Worrall, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1609.